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(11) EP 0 790 244 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of Publication
23.08.1997 Patentblatt 1997/34(51) Int. Cl.⁴: C07D 285/14, C07C 255/03,
C11D 1/58, C11D 1/62,
C11D 3/39

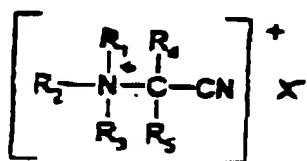
(21) Appn. No.: 97101830.4

(22) Filed: 06.02.1997

(84) Designated National States
AT BE CH DE DK ES FR GB IT LI NL PT SE(30) Priority Date
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(54) Ammonium Nitriles and their use as Bleach Activators

(57) Ammonium Nitriles of the general formula:



in which the R_1 and R_2 residues together with the nitrogen atom form a heterocycle. R_3 is an organic substituent, R_4 and R_5 are either hydrogen or other organic substituents, R_3 is preferably a lower alkyl residue, R_4 and R_5 are preferably hydrogen, and X is an appropriate anion. The compounds of the invention are to be used as bleach activators in bleaching detergents and cleaners.

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Description

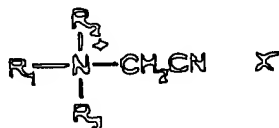
This invention concerns ammonium nitriles and detergent compositions which contain these nitriles as bleach activators.

It is known that the bleaching potential of peroxygen bleach compounds, such as perborate, percarbonate, persulfate and perphosphate can be improved so that effective bleaching can occur at lower temperatures (at or under 60°C). This is accomplished by using the precursors of peroxyacids, which are often referred to as bleach activators.

There are many such examples of compounds in the prior art known as bleach activators. Typical examples are reactive organic compounds with either an O-Acyl or N-Acyl group, which generates a corresponding peroxyacid, when the compound is combined in alkaline solution with a source of hydrogen peroxide.

Representative examples of such bleach activators are N, N, N', N'-tetraacetylenediamine (TAED), glucose pentaacetate (GPA), Xylose tetraacetate (TAX), sodium-4-benzoyloxybenzenesulfonate (SBOBS). Sodium trimethylhexanoyloxybenzene sulfonate (STHOBS), tetraacetylglycoluril (TAGU), tetraacetylcyanuric acid (TACA), di-N-acetyldimethylglycouril (ADMG) and 1-phenyl-3-acetylhydantoin (PAH). Exemplary activators are disclosed in GB-A-836,988, GB-A-907356, EP-A-0 098 129 and EP-A-0 120 591. In meanwhile, cationic bleach activators, which contain a quaternary ammonium group, have attained significance as highly effective bleach activators. Examples of such cationic bleach activators are found in GB-A-1392594, U.S. 4,751,015, EP-A-0 284 292 and EP-A-0 331 229.

Ammonium nitriles of the formula



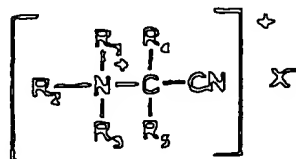
form a special class of cationic bleach activators. Compounds of these types and their use as bleach activators in bleach compositions are described in EP-A-303 520, EP-A-464 880, EP-A-458 396 and U.S. 4,883,917. In all of the compounds described in these references, the nitrogen atom of the ammonium group is substituted exclusively with alkyl, alkenyl or aryl groups.

It appears that these compounds form in perhydrolysis a peroxyimide acid, which is the bleaching agent.

It has now been surprisingly found that ammonium nitriles as above described, which are derived from cyclic amines, perform better as bleach activators than other nitriles found in the prior art.

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The object of the invention comprises compounds of the general formula:



in which R_1 and R_2 together with the nitrogen atom to which they are attached form a ring with four to six carbon atoms, which can be substituted with C_{1-5} alkyl, C_{1-5} alkoxy, C_{1-5} alkanoyl, phenyl, amino, ammonium, cyano, cyanoamino, chloride or bromide, and whereby these ring may also contain, in addition to the nitrogen atom, and in place of the carbon atoms, 1 or 2 oxygen or nitrogen atoms, and NR_6 group or a R_5-N-R_6 group, in which R_6 is hydrogen, C_{1-5} alkyl, C_{2-5} alkylaryl, C_{2-5} alkynyl, phenyl, C_{7-9} arylalkyl, C_{5-7} cycloalkyl, C_{1-5} alkanoyl, cyanomethyl or cyanide. R_3 is a C_{1-24} , preferably C_{1-4} alkyl, C_{2-24} , preferably C_{2-4} alkenyl, cyanomethyl or C_{1-4} alkoxy- C_{1-4} alkyl, R_4 and R_5 are hydrogen C_{1-4} alkyl, C_{1-4} alkenyl, C_{1-4} alkoxy- C_{1-4} alkyl, phenyl or C_{1-3} alkylphenyl, preferably hydrogen, methyl or phenyl in which it is especially preferred that R_4 is hydrogen and R_5 is not hydrogen, and X is an anion, preferably chloride, bromide, iodide, fluoride, sulfate, hydrogen sulfate (bisulfate), carbonate, hydrogen carbonate (bicarbonate), phosphate, mono- and di hydrogen phosphate, pyrophosphate, metaphosphate, nitrate, methosulfate, dodecylsulfate, dodecylbenzene, sulfonate, phosphonate, methylphosphonate, methane disulfonate, methylsulfonate, or ethane sulfonate. Especially preferred compounds, which are all good peroxygen activators and which possess good stability are cyclic ammonium-N-(cyanomethyl)-N-methyl chloride-sulfate with 5-8 ring atoms, which can additionally contain oxygen and/or nitrogen, especially morpholinium-N-(cyanomethyl)-N-methylchloride, N-pyrrolidinium-N-(cyanomethyl)-N-methylchloride and piperazinum-N,N'-(dicyanomethyl)-N,N'-dimethylchloride.

The cationic nitriles of the invention can be synthesized in accordance with the following common examples.

1. A cyclic, secondary amine, sodium cyanide and formaldehyde, preferably 38% formalin, are added together in an ethanol/water mixture. After a reaction time of 3-7 hours at a temperature between 10-30°C, preferably at 25°C, aqueous hydrochloric acid is added to the mixture. The aqueous phase is extracted with an appropriate organic solvent, e.g., methylene chloride. The solvent is then removed from the remaining organic phase. The resulting aminoacetonitrile is dissolved in an organic solvent and reacted with a methylating agent like methyl chloride or dimethylsulfate at a temperature between 20° and 100°C, preferably between 70° and 80°C, to form the corresponding ammonium-N-(cyanomethyl)-N-methyl salt.

2. A cyclic, secondary amine and sodium hydroxide are dissolved in a toluene/water mixture and chloroacetonitrile is added dropwise at a temperature between 5 and 30°C, preferably at 10 to 15°C.

After 2-5 hours reaction time, the organic phase is divided, and the aqueous phase is extracted with an organic solvent. The solvent is withdrawn from the remaining organic phase. The resulting aminoacetonitrile is taken up in an organic solvent and reacted with a methylating agent like methylene chloride or

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dimethylsulfate at a temperature between 20° and 100°C, preferably 70° and 80°C, in order to form the corresponding ammonium-N-(cyanomethyl)-N-methyl salt.

3. A cyclic, tertiary amine and chloroacetonitrile are reacted in an appropriate solvent, e.g., acetone, for 3-7 hours at a temperature between 10° and 30°C, preferably at 25°C. The resulting precipitate is recovered by filtration, and is the corresponding cyclic ammonium-N-(cyanomethyl)-N-methylchloride.

It also an object of the invention to use these ammonium nitriles as bleach activators in bleaching detergents and cleaning compositions. These detergents and cleaning compositions contain, in addition to a peroxygen compound, and the cationic, nitrile bleach activators preferably additional surface active materials and further well known adjunct materials.

Suitable peroxygen bleaching compounds are alkaline peroxides, organic peroxide such as urea peroxide and inorganic persalts, such as alkali metal perborate, alkali metal percarbonates, alkali metal perphosphates, alkali persilicas and alkali metal persulfates. Mixtures of two or more of these compounds are also suitable. Especially preferred are sodium perborate tetrahydrate, and especially, sodium perborate monohydrate. Sodium perborate monohydrate is most preferred because of its good storage stability and good solubility in water. Environmental concerns also favor the use of sodium percarbonate. Alkyl hydroperoxide are a further preferred class of peroxygen compounds. Examples of these materials are cumene hydroperoxide and t-butyl hydroperoxide.

The cationic, nitrile bleach activator of the invention can be present in detergent and cleaning compositions in an amount by weight of about 0.1-20%, preferably 0.5-10%, and especially of about 1-7.5%, together with a peroxygen compound. The peroxygen compound should be present in an amount by weight of usually between 2-40%, preferably 4-30%, and especial 10-25%.

Still further appropriate bleach activators, such as e.g., TAED, can be present in addition to the cationic, nitrile bleach activators of the invention in detergent and cleaning compositions.

The surface active compound can be derived from natural products, such as soap, or is a synthetic compound selected from the group consisting of anionic, nonionic, amphoteric, zwitterionic or cationic surface active compounds, or mixtures thereof. Many suitable compounds are commercially available and are described in the literature, for example, in Schwartz, Perry and Berch, "Surface Active Agents and Detergents,) Vols. 1-2. The surface active compounds may be present in these compositions by weight from up to 50%, preferably 1-40%, and especially 4-25%. Synthetic anionic surfactants are typically water soluble alkali metal salts of organic sulfate and sulfonates with alkyl residues of about 8-22 carbon atoms, in which the expression "alkyl" includes alkyl substituents of a higher aryl residue.

Examples of suitable anionic detergents are sodium and ammonium alkyl sulfates, especially the alcohol sulfate which results from the sulfation of higher (C₈-C₁₆) alcohol; sodium and ammonium alkyl benzenesulfonates with an alkyl residue of C₉-C₂₀, especially linear secondary sodium alkyl benzenesulfonates with an alkyl residue of C₁₀ - C₁₅; sodium alkyl glycol ether sulfates, especially the esters of higher alcohols such as those derived from palm and coconut oils; the sodium sulfates and sodium sulfonates of monoglycerides of coconut fatty acid; sodium and ammonium salts of sulfuric acid esters of higher (C₈- C₁₅) fatty alcohols, especially those which have been oxyalkylated with ethylene oxides, the reactions products of the esterification of fatty acids with (methionic ?) acid and succeeding neutralization with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl

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taurine; alkane monosulfates such as those from the reaction of C_{8-20} alpha-olefins with sodium sulfite and those from the reaction of paraffins with SO_2 and Cl_2 with successive alkaline basic hydrolysis, whereby a mixture of different sulfonates results; sodium and ammonium alkyl sulfosuccinates with alkyl residues of C_{7-12} ; and olefin sulfonates, which result from the reaction of olefins (especially C_{10-20} alpha-olefins) with SO_2 and successive hydrolysis of the reaction products. The preferred anionic detergents are sodium alkyl benzenesulfonates with alkyl residues of C_{15-18} and sodium alkyl ethersulfates with alkyl residues of C_{10-18} .

Examples of suitable nonionic surfactants, which are preferably used together with anionic surfactants, are preferably the reactions products of alkylene oxides (usually ethylene oxide or, EO) with alkylphenols (alkyl residues of C_{8-22}), in which the reaction products contain in general, 5-25 ethylene oxide groups per molecule; the reaction products of aliphatic (C_{8-16}) primary or secondary, linear or branched alcohols with ethylene oxide, with generally 6-30 EO groups; and the addition products of ethylene oxide with reaction products of propylene oxide and ethylene diamine. Other nonionic surfactants are alkylpolyglycosides, long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkylsulfoxides.

Amphoteric or zwitterionic surfactants can also be used in the compositions of the invention, but because of their higher cost, are generally not preferred. If amphoteric or zwitterionic compounds are used, they will be generally added in some amount of formulations which will mainly contain anionic and nonionic surfactants.

Soaps can also be used in the composition of the invention, preferably in an amount by weight of less than 25%. They are especially suitable in small quantities in binary (soap/anionic surfactant) mixture or in ternary mixtures together with nonionic or mixed synthetic anionic and nonionic surfactants. The suitable soaps are preferably the sodium salts, and less preferably the potassium salts, of saturated or unsaturated C_{10-24} fatty acids, or mixtures thereof. The amount of such soaps can be from 0.5-25% by weight with lesser amounts of 0.5-5% viewed as preferable in order to control foam. It is advantageous to have a soap content of between 2-20%, especially between 5 and 10%. This is especially the case in hard water situations, in which the soap functions as an additional builder.

The detergent and cleaning compositions of the invention contain in general at least one builder. These builders include calcium binding materials, precipitating compounds, calcium specific ionic exchange materials, and mixtures thereof. Examples of calcium binding materials include alkali metal polyphosphates, such sodium tripolyphosphate; nitrilotriacetic acid and its water soluble salts; the alkali metal salts of carboxymethylloxysuccinates, ethylenediaminetetraacetic acid, oxysuccinates, mellitic acid, benzenepolycarboxylic acid, and citric acid; and polyacetalcarboxylate, such as those disclosed in U.S. Patents 4,144,226 and 4,146,495.

Examples of precipitating agents includes sodium orthophosphate, sodium carbonate and soaps of long chain fatty acids.

Examples of ionic exchange materials, which are specific for calcium, include the different types of water insoluble, crystalline or amorphous aluminosilicates, of which zeolites are the most well known representatives.

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These builders may be present in an amount of 5-80% by weight, preferably in an amount of 10-60%.

Besides these already mentioned ingredients, the detergent and cleaning compositions of the invention can include the conventional adjunct materials in amounts which are usually found in such compositions. Examples of these adjunct materials include foam controllers, such as alkanolamides, especially monoethanolamides of palm oil fatty acids and coconut fatty acids; foam hindering agents, such as alkylphosphates and alkylsilicones; detergency boosters, such as sodium carboxymethylcellulose and alkyl or substituted alkyl cellulose ethers; stabilizers, such as EDTA; fabric softeners; inorganic salts, such as sodium sulfate; and, in appropriately small quantities, fluorescent whiteners, perfumes, enzymes, such as protease, cellulase, lipase and amylase, disinfectants and colorants/dyes. The bleach activators of this invention can be added to a variety of different products. These include laundry detergents, laundry bleaches, hard surface cleaners, toilet cleaners, automatic dishwasher detergents, and denture cleaners. These detergents can be in solid or liquid form.

For reason of stability and handleability, it is advantageous to execute the bleach activators in the form of granules, in which the bleach activators are combined with a binding material. There are many different methods for preparing these granules, as described in the patent literature, for example in Canadian Pat. No. 1,102,966, GB-1,561,333, U.S. 4,087,369, EP-A-0 240057, EP-A-0 241962, EP-A-0 101634 and EP-A-0 062523. Any of these methods are applicable to the bleach activators of the invention.

Granules which contain the bleach activators of the invention will in general will be added to the detergent formulations with other, dry ingredients such as enzymes and inorganic peroxygen bleaches. The detergent formulations, to which the activator granules will be added, can be prepared in numerous different ways, such as dry mixing, extrusion, or spray drying.

In a further execution, the bleach activators of the invention are especially appropriate for nonwater soluble detergents, together with a bleaching peroxygen compound, such as sodium perborate, in order to provide concentrated cleaning performance for fabrics and textiles. These types of nonaqueous, liquid detergents, which include paste and gel detergents, are known in the prior art and are described for example in U.S. 2,564,770, U.S. 2,940,958, U.S. 4,772,412, U.S. 3,365,877, GB-A-1205711, GB-A-1370377, GB-A-1270040, GB-A-1282362, GB-A-2194536, DE-A-2233771, EP-A-0 028849.

Some of these compositions can be in the form of a nonaqueous, liquid medium, in which a solid phase is dispersed. The nonaqueous, liquid medium can be a liquid surfactant, preferably a nonionic surfactant; a nonpolar liquid medium such as liquid paraffin; a polar solvent, such as various polyols, for example, glycerin, sorbitol, ethylene glycol, possibly together with lower molecular weight monoalcohols, such as ethanol or isopropanol; or mixtures thereof.

The solid phase can consist of builders, alkaline materials, abrasive materials, polymers, ionic materials, other solid ionic surface active materials, bleaches, fluorescent whiteners, and other, typical solid ingredients.

The following non-limiting examples give an overview of various executions of the invention.

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Example 1: Synthesis of piperidine acetonitrile

40.6g 36% formalin solution is added dropwise to 42.6g room temperature piperidine, in an ice bath. After thinning the resulting viscous reaction mixture with 50ml water and 50ml ethanol, 24.4g sodium cyanide is thereafter added. The reaction mixture is then stirred for 2-3 hours at room temperature, after which 58.5 g 31% hydrochloric acid is added with cooling. The aqueous phase is then extracted with methylene chloride, the organic phases are unified, and solvent is removed under vacuum. 59.4 g piperidine acetonitrile is obtained, which represents a 96% yield.

Example 2: Synthesis of piperidine acetonitrile

50ml water and 50ml toluene are mixed at 10-15°C. 21g sodium hydroxide is added with cooling. After cooling down to 10-15°C, 43.4g piperidine is added, and thereafter, 37.8g chloroacetonitrile is added dropwise with cooling within 1.5 hours. The viscous reaction mixture is allowed to stand overnight, and the aqueous phase can be removed with toluene. The solvent is removed from the unified organic phase. 53.6g piperidine acetonitrile is obtained, which represents an 85% yield.

Example 3: Synthesis of hexamethyleneimine acetonitrile

50ml water, 50ml methylene chloride and 21g sodium hydroxide are mixed at 15°C. Contemporaneously 49.8g hexamethyleneimine are added at 10-15°C, and thereafter, 37.8g chloroacetonitrile is added dropwise in 1.5 hours. The mixture is stirred for 5 hours, the aqueous phase is divided with methylene chloride, and the solvent is removed from the combined organic phase. 64.9g hexamethyleneimine acetonitrile is obtained, which represents a 94% yield.

Example 4: Synthesis of piperidinium-N-(cyanomethyl)-N-methylchloride

50g acetone and 38.8g chloroacetonitrile are mixed at room temperature, and then 49.6g 1-methylpiperidine are drop wise added in 1 hour. Because the resulting white precipitate will make the mixture very viscous, 100ml acetone must be added to thin the mixture after about 1.5 hours. After completion of the reaction, the product is sucked off and wash with acetone. 80.3g piperidine-N-(cyanomethyl)-N-methylchloride is obtained, which represents a 92% yield.

Example 5: Synthesis of pyrrolidinium-N-(cyanomethyl)-N-methylchloride

50ml acetone and 38.8g chloroacetonitrile are mixed. To this mixture, 43.9 g N-methylpyrrolidone is added within 1.5 hours at 25°C, with cooling. The reaction mixture will look muddy and viscous. After 5 hours stirring, the product is sucked off and washed with acetone. 76g pyrrolidinium-N-(cyanomethyl)-N-methylchloride is obtained, which represent a 95% yield.

Example 6: Synthesis of piperidinium-N-(cyanomethyl)-N-methylchloride

124g piperidine acetonitrile is dissolved in 180g isopropanol and placed in an autoclave. Methylene chloride is added at a temperature of 70-80°C at a pressure of 4-5 bars, with a reaction time of 24 hours. Towards the end of the reaction, a viscous solution is obtained which is removed under vacuum. The product is obtained in quantitative yields.

Example 7:

A bleach detergent composition is produced by combining 200ml from an aqueous solution of 5 g/l of reference detergent (WMP), received from WFK-Testgewebe GmbH, Krefeld, Germany); 150mg sodium perborate monohydrate (PB1); and 50mg of a bleach activator. Four swatches (BC-1-tea on cotton, 1.25g WFK) soiled with black tea are added to a Linitest-apparatus for a 30 minute, isothermic wash experiment. After the prescribed wash time, the fabric swatches are then rinsed with water, dried

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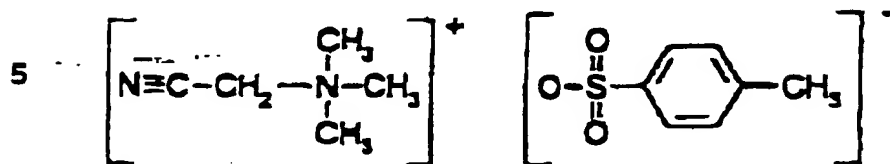
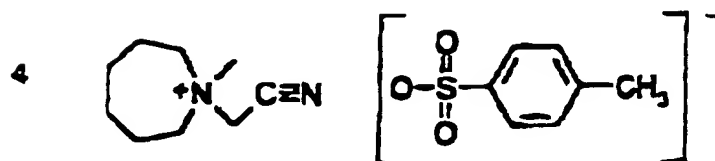
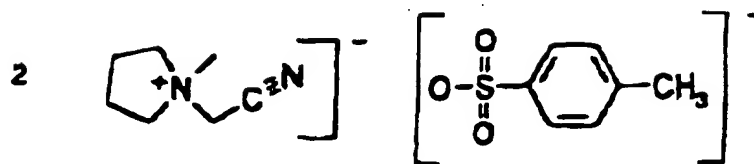


Table 1

Alkylator No.	ΔR (Quat)	ΔR (Quat + TAED)	$\Delta\Delta R$ (Quat - PB ¹)	$\Delta\Delta R$ (Quat - TAED)	$\Delta\Delta R$ (Quat - PB ¹)	$\Delta\Delta R$ (Quat - TAED)
PB ¹	11,8					
TAED		14,55				
1	23,5	25,2	12,2	11,8	15,4	14,7
2	22,5	27,1	11,2	12,5	13,3	14,9
3	20,2	22,5	8,9	8,0	12,1	9,9
4	21,0	24,1	9,7	9,5	12,5	12,4
5	20,8	21,6	9,5	7,1	10,3	7,6

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and ironed. Contemporaneously, bleaching performance is ascertained by using an Elrepho 2000 (Datacolor) machine, by which the differences in remissions before and after bleaching are measured.

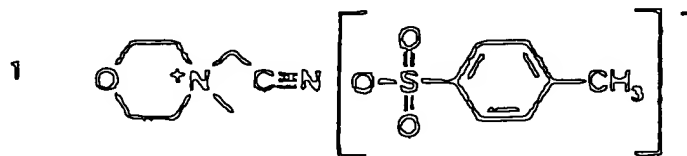
The experiment is repeated by using different soils (e.g., grass, curry) and at differing temperatures (20°C, 40°C). Comparative experiments were all conducted in which 50mg TAED was added to bleaching detergent compositions. The experiments were also repeated by using 0.2 mmol activator from time to time.

Bleaching detergent compositions were prepared which had organic peracid precursors 1-4 and the comparative activator 5, as portrayed in Table I. The activators' bleaching performance was measured by comparing the remission of the fabric swatches before and after treatment with bleach. The results are depicted in Table I. The $\Delta\Delta R$ - values depict the improvement of bleaching performance by the compositions of the invention compared against PB*1 and TAED:

$$\Delta\Delta R \text{ QUAT} - \text{PB}^*1 = \Delta R(\text{QUAT}) - \Delta R(\text{PB}^*1)$$

$$\Delta\Delta R \text{ QUAT} - \text{TAED} = \Delta R(\text{QUAT} + \text{TAED}) - \Delta R \text{ TAED}$$

the compounds 1 to 5 are depicted below:



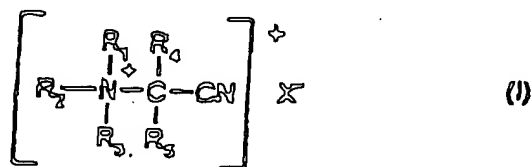
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The first 4 columns of Table I describe the addition of 50mg activator, while the last 2 columns concern the addition of 0.2 mmol activator.

The strongest bleaching performance occurred at pH 9.5 to 10. A comparison of the Δ -R values for the novel cationic nitriles demonstrated that the best soil removal occurred at the preferred pH values between 7-12.

Further useful characteristics of cationic nitriles are minimal dye damage and minimal fiber damage. Experiments with colored fibers (Remazol™ red granule 133 and Remazol™ black B) demonstrated that activator 1 caused the least amount of color damage.

Patent Claims



1. Compounds of the general formula I in which R_1 and R_2 together with the nitrogen atom to which they are attached form a ring with four to six carbon atoms, which can be substituted with C_{1-5} alkyl, C_{1-5} alkoxy, C_{1-5} alkanoyl, phenyl, amino, ammonium, cyano, cyanoamino, chloride or bromide, and whereby these ring may also contain, in addition to the nitrogen atom, and in place of the carbon atoms, 1 or 2 oxygen or nitrogen atoms; an NR_6 group or a R_3 -N- R_6 group, in which R_6 is hydrogen, C_{1-5} alkyl, C_{2-5} alkylaryl, C_{2-5} alkynyl, phenyl, C_{7-9} arylalkyl, C_{5-7} cycloalkyl, C_{1-5} alkanoyl, cyanomethyl or cyanide; R_3 is a C_{1-20} , preferably C_{1-4} alkyl, C_{2-20} , preferably C_{2-4} alkenyl, cyanomethyl or C_{1-4} alkoxy- C_{1-4} alkyl, R_4 and R_5 are hydrogen C_{1-4} alkyl, C_{1-4} alkenyl, C_{1-4} alkoxy- C_{1-4} alkyl, phenyl or C_{1-3} alkylphenyl, preferably hydrogen, methyl or phenyl in which it is especially preferred that R_4 is hydrogen and R_5 is not hydrogen, and X is an anion.

2. Compounds of the general formula I of Claim 1, further characterized in that R_1 and R_2 together with nitrogen atom to which they are attached form a ring with 5 or 6 carbon atoms, wherein a carbon atom can be replaced by an oxygen atom or a N- R_6 group, in which R_6 is cyanomethyl, R_3 is C_{1-4} alkyl, R_4 and R_5 is hydrogen, and X is an anion.

3. Compounds of the general formula according to Claim 1, further characterized in that R_1 and R_2 together with the nitrogen atom to which they are bound form a pyrrolidine, morpholine, piperidine or a N-cyanomethyl N'-methylpiperazinum ring, R_3 is C_{1-2} alkyl, R_4 and R_5 are hydrogen, and X is an anion.

4. Detergent and cleaning compositions containing a peroxygen compound and compound of the formula I as in Claim 1.

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EUROPEAN SEARCH REPORT

Europatent
Patentamt

Nummer der Anmeldung

EP 97 10 1830

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION DES ANMELDUNG GULC
Category	Citation of document with indication, where appropriate, of relevant passage	Claims	
P.X	WO 96 48661 A (THE CLOROX COMPANY) 19. Dezember 1996 * Claims 1-44 *	1-4	C07D295/14 C07C255/03 C11D1/58 C11D1/62 C11D3/39
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-/-			
Der vorliegende Suchsuchbericht wurde für die Patentanmeldung erstellt			
MÜNCHEN		18. Juni 1997	Herz, C
KATEGORIE DER GEMAPOTEN DOCUMENTE			
X: von besonderer Bedeutung als Priorität V: von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung desselben Erfinders A: wissenschaftlicher Hintergrund O: ökonomische Informationen F: Fachliteratur		T: zur Erklärung wichtiger Begriffe Theorie oder Grundlagen E: Erfindungsbereich, der jedoch nicht mit einer neuen Ausgestaltung verbunden ist D: in der Anmeldung vorgeschlagene Dokumente L: aus anderen Quellen abgeleitete Dokumente A: Material der gleichen Priorität, nicht eingereicht Dokument	

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EUROPÄISCHER RECHERCHENBERICHT

Nummer der Anmeldung
EP 97 10 1830

EINSCHLÄGIGE DOKUMENTE		
Kategorie	Kennzeichnung des Dokuments als Angabe, wonach ermittelt, ob einschlägiges Tech.	Recherchierter Bereich
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		BEZUGNEHME SACHVERHALT (SACHV.)
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MÜNCHEN	18. Juni 1997	Herz, C
KATEGORIE DER EINGETRAGENEN DOKUMENTE		
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